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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Reactive Hot Melt Systems Containing Isocyanate Groups**

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Notice: This application is as filed and may therefore contain an incomplete specification.



Reactive hot melt systems containing isocyanate groups**A B S T R A C T**

Reactive hot melt systems containing isocyanate groups, based on hydroxypolyols containing ester and/or ether groupings with a hydroxyl number of 15 to 150 and an average functionality of 1.95 to 2.2, and diphenylmethane diisocyanates, with a ratio of isocyanate groups in the diphenylmethane diisocyanates to hydroxyl groups in the polyols of 1.4:1 to 2.5:1, which have a content of at least 70 weight % of 2,4'-diphenylmethane diisocyanate, are characterized by a low initial viscosity and enhanced temperature stability and are suitable as solid adhesives for very different areas of use.

Reactive hot melt systems containing isocyanate groups

5 This invention relates to reactive hot melt systems containing isocyanate groups which have a low initial viscosity and enhanced temperature stability comprising hydroxypolyols having ester and/or ether groupings and special diphenylmethane diisocyanates, and relates to their use as adhesives in very different areas of use.

10 Joining processes employing solvent-free adhesive systems containing 100% solids are currently becoming increasingly important, because the use of solvent-containing systems necessitates costly solvent recovery installations and the use of aqueous dispersion or solvent systems necessitates evaporation of the water, which is likewise very cost-intensive. Melt adhesives, which have long been known, provide a technical
15 alternative. Their advantages are that they are applied as hot melts which rapidly solidify on cooling and thereby develop strength. A disadvantage is that the adhesive bonding of substances which are temperature-sensitive is made difficult due to the high melting temperatures, and since the applied adhesive, unless it is further processed immediately, transforms due to its rapid solidification into a state in which wetting is no longer taking place and which can only be thermally activated again under extreme conditions of temperature. Moreover the bond has a limited hot strength on account
20 of the thermoplastic character of the hot melt.

25 One elegant manner of providing the property of melt adhesives, namely of the development of strength on cooling, and at the same time enabling them to be applied at low temperatures whilst obtaining adhesive bonds of good hot strength, is a joining procedure described in principle in DE-OS 2 609 266 which employs reactive hot melt systems based on isocyanate-containing prepolymers of diisocyanates and polyester diols having melting ranges above 40°C. Due to their low molecular weights, the products are fluid and workable at temperatures a little above the melting range of the polyester. After a chain-lengthening reaction which proceeds on the substrate they
30 attain an adequate molecular weight, which together with the recrystallisation of the crystalline polyester chain segments results in an increased initial strength. The final

strength is reached by the complete reaction of the free isocyanate groups which are still present with atmospheric moisture, for example, with the formation of linear, high molecular weight polyurethane polyureas.

5 The problem of achieving a balance between the property of the highest possible initial strength and the lowest possible temperature of application or melting of reactive hot melt systems has not yet been solved completely satisfactorily. Systems containing isocyanate groups become increasingly unstable at the elevated temperatures required for their viscosity on application, even if atmospheric moisture is excluded. This is
10 discernible by a sharp increase in viscosity, and in extreme cases by gelling of the melts. This results in caking in melting vessels and metering devices, which can only be cleaned again at high cost.

15 It would therefore be desirable if hot melt systems containing isocyanate groups were available which had an enhanced thermal stability, which could be held in the molten state for a long period at high temperatures without irreversibly transforming into the gel state or exhibiting a sharp increase in viscosity.

20 Surprisingly, it has now been found that when certain polyisocyanates are used hot melt systems can be obtained which exhibit a significantly enhanced stability of their viscosity without their other properties being impaired.

25 Accordingly, the present invention relates to reactive hot melt systems containing isocyanate groups having a low initial viscosity and enhanced temperature stability, comprising

(i) hydroxypolyols containing ester and/or ether groupings, with a hydroxyl number of 15 to 150 and an average functionality of 1.95 to 2.2, and

(ii) diphenylmethane diisocyanates

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with a ratio of isocyanate groups in (ii) to hydroxyl groups in (i) of 1.4:1 to 2.5:1, which are characterized in that diphenylmethane diisocyanates are used which have a content of at least 70 weight % of 2,4'-isomers.

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The polyols (i) which are used comprise the hydroxyl compounds which are commonly used in polyurethane chemistry, for example such as polyether polyols which are preferably based on bifunctional starters, e.g. propylene glycol or 2,2-bis-4-hydroxyphenylpropane, and propylene oxide which preferably has a hydroxyl number of 20 to 150. Proportions (5 to 20 weight %, based on (i)) of polyols of higher functionality may also be used conjointly, such as propylene oxide polyether polyols started with trimethylolpropane which have a hydroxyl number from 30 to 500, for example. When polyols of higher functionality are used conjointly, the hydroxyl number of hydroxypolyols (i) may increase to a value of 180, preferably 160.

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The use of crystalline or amorphous hydroxylpolyesters as polyols (i) is preferred. Crystalline polyester polyols are to be understood as those which exhibit an endothermic maximum above room temperature on differential thermal analysis (DTA). Amorphous polyester polyols are to be understood as those which exhibit no endothermic maximum above room temperature on differential thermal analysis.

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Esterification products of adipic acid or dodecane diacid, of ortho-, iso- or terephthalic acid, of carbonic acid or of dimeric fatty acid (polycarboxylic acids obtained by the dimerization of unsaturated fatty acids (e.g. oleic acid)) with glycols, such as ethylene glycol, 1,4-butanediol or 1,6-hexanediol, for example, are preferably used as the

polyester polyols having hydroxyl numbers from 15 to 100, preferably 20 to 75. Mixtures of acids and/or glycols may also of course be used. The proportional use in conjunction of trimethylolpropane, for example, is also possible. In addition to the above-mentioned dicarboxylic acids, the use of hydroxycaproic acid or caprolactone is also possible.

The preparation of polyether- and polyester polyols (i) is known and is described, for example, in Ullmanns Encyklopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], "Polyesters", Fourth Edition, Verlag Chemie, Weinheim, 1980.

Di-, tri- and/or tetraethylene glycol, 1,4-dimethylolcyclohexane or trimethylolpropane or reaction products of 4,4'-hydroxyphenylpropane with ethylene- and/or propylene oxide should be cited as low molecular weight hydroxyl compounds which are optionally to be used conjointly with component (i). Diols containing ions or components which form ionic groups, such as dimethylolpropionic acid, N-methyl diethanolamine and/or reaction products of sodium bisulphite with propoxylated 1,4-butenediol, for example, may also of course be used for special effects. The amount of low molecular weight hydroxyl compounds is preferably 0.01 to 0.5 moles per mole of component (i).

Polyester polyols and polyether polyols (i) preferably have an average functionality of 1.95 to 2.05.

According to the invention, diphenylmethane diisocyanates (ii) are used which have a content of at least 70 weight %, preferably of at least 85 weight %, of 2,4'-isomers.

Diphenylmethane diisocyanates (ii) such as these may be prepared by various methods, such as the distillation of an industrial diphenylmethane diisocyanate mixture, for example.

The ratio of hydroxyl groups in polyol components (i) to isocyanate groups in diisocyanates (ii) is preferably 1:1.5 to 1:2.0.

5 The hot melt systems containing isocyanate groups are prepared, for example, by mixing the liquid polyols with an excess of polyisocyanates, whereupon the homogeneous mixture is drawn off or is stirred until a constant NCO value is reached, which is mostly achieved after two hours, and is then drawn off. A temperature of 60 to 150°C, preferably 65 to 110°C, is selected as the reaction temperature. The preparation of the reactive hot melt may also of course be carried out continuously in 10 a cascade of stirred vessels or in suitable mixing units, such as high-speed mixers based on the rotor-stator principle, for example.

It is of course possible to modify the polyester- and/or polyether polyols or part of the same with a deficit of diisocyanates, preferably hexamethylene diisocyanate, and to 15 react the polyols containing urethane groups, after this reaction is complete, with an excess of diisocyanates to form a hot melt containing isocyanate groups.

It is also possible to conduct the reaction of the polyols with the diisocyanates in the presence of up to 5 weight % of trimers of aliphatic diisocyanates, for example, such 20 as hexamethylene diisocyanate for example, or to add trimers such as these after the completion of prepolymerization.

The hot melt systems have an almost unlimited storage life when they are stored at room temperatures up to 40°C with the exclusion of moisture. They can be modified 25 in the usual manner with inorganic or organic fillers, colorants, resins and/or extender oils and constitute excellent adhesives.

They are applied at an elevated temperature, wherein the hot melt systems are melted continuously or batch-wise at temperatures of 80 to 160°C and the melts are brought

into contact with the substrates to be adhesively bonded. Bonding is firstly effected physically due to the increase in viscosity or by recrystallization of the polyester segments, and is effected later by chemical reaction of the isocyanate groups with moisture or other Zerewitinoff-active groups, e.g. with glycols.

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The substrate and atmospheric moisture are normally sufficient for bonding, but the reaction may of course be accelerated by providing an additional misting with media containing water, glycols or catalysts, such as water vapour containing triethylamine.

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Compared with systems based on conventional diphenylmethane diisocyanates of comparable molar compositions, hot melt systems of the type claimed are distinguished by a lower viscosity and, particularly when crystalline polyester polyols are used, by their more rapid crystallization and thus by their more rapid initial solidification or shorter "open time", as described in DE 3 931 845 for example. In particular,

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however, the thermal stability of the systems is significantly improved and thus constitutes a technical advance which makes the class comprising these hot melt systems even more attractive. Moreover it is now possible to produce hot melts

containing isocyanate groups based on very viscous polyester polyols, which can be used, despite the requisite high processing temperatures, without the very disadvantageous sharp increase in viscosity which occurred hitherto during processing.

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In particular, considerably improved reactive hot melt adhesives are thus accessible for the adhesive bonding of valve bags. They solve the problem which existed hitherto,

which consists of the combination of properties which are actually mutually exclusive which is required for trouble-free production, namely a very high viscosity or abrasion-

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resistance of the applied adhesive film for compounds which provide very good stability of viscosity of the adhesive which is present at very high temperatures in the melt application vessel and in the applicator unit.

In the same manner, the production of technically improved reactive hot melt adhesives for composite film manufacture is also possible.

5 The hot melt systems according to the invention can be used as adhesives for a diversity of applications, for example as a mounting adhesive for the preliminary fixing of components, as a bookbinding adhesive, or as adhesives for the manufacture of valve bags, composite films or laminates.

Examples**Polyester polyols**

- 5 A-1 A crystalline hydroxyl polyester of adipic acid and 1,6-hexanediol: hydroxyl number 28.0, acid number 0.6, average functionality 2.0
- 10 A-2 An amorphous hydroxyl polyester of neopentyl glycol and a mixture of adipic acid and isophthalic acid in a 6:4 molar ratio:
hydroxyl number 56.2, acid number 0.7, average functionality 2.0
- 15 A-3 An amorphous hydroxyl polyester, Dynacoll 7210 manufactured by Hüls AG, with a hydroxyl number of 33 and an average functionality of 2.0
- 15 A-4 An amorphous hydroxyl polyester, Dynacoll 7110 manufactured by Hüls AG, with a hydroxyl number of 52 and an average functionality of 2.0

Diisocyanates

- 20 C-1 A diisocyanatodiphenylmethane mixture containing 87.1 % 2,4'-, 11.2 % 4,4'- and 1.7 % 2,2'-isomers
- 20 C-1A A diisocyanatodiphenylmethane mixture containing 77.0 % 2,4'-, 22 % 4,4'- and 1 % 2,2'-isomers
- 20 C-2 4,4'-diisocyanatodiphenylmethane (100 %).

Preparation of prepolymers

- 25 The molten polyols were dehydrated for 60 minutes at 100°C and at about 20 mbar with stirring.

The diisocyanate was added at about 80 to 90°C and stirred under nitrogen until a constant isocyanate content was obtained.

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The prepolymer was introduced into cartridges.

Investigation of the hot melt systems

- 5 After storage for two weeks at room temperature the cartridges were melted at 130 to 140°C for 60 minutes in an oven.

The isocyanate content of the liquid prepolymer was determined by titration with dibutylamine.

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- The liquid hot melt was applied to beechwood test pieces and its curing characteristics were determined using a "CUREM" (see DE 3 931 845), divided into a wetting phase A (seconds) and a crystallization phase B (seconds). For this purpose the adhesive in the joint gap of the materials to be adhesively bonded was subjected to sinusoidally alternating shear loading, and the shear forces thus arising were continuously measured. The measured shear forces were displayed as a function of time (in seconds). The shear was produced via a frequency-controlled thrust motor and a fine threaded spindle. The displacement was 200 µm, and the loading frequency was 1 Hz. The joint gap measured 0.2 mm and the temperature of the test piece clamping jaws was set at 20±2°C. Measurements were recorded for 10 minutes.
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The cohesion strength was determined on the beechwood test pieces (after 24 hours and after 7 days) [see Table 2].

Testing the storage stability (Table 3)

The hot melt systems were melted at 120°C in aluminium cartridges and stored for 24 hours or 72 hours. Viscosities were determined at 120°C at a shear rate of $D = 50 \text{ l/s}$ using an MC-10 cone/plate viscometer (manufactured by Physika).

Table 1

	(moles) Pol-A	moles TMP*	(moles) dilso. C	NCO/OH	% NCO
1	1.0 A-1	/	1.9 C-1	1.9	1.69
1 A	1.0 A-1	/	1.9 C-2	1.9	1.59
2	1.0 A-1	0.25	2.61 C-1	1.9	1.99
2 A	1.0 A-1	0.25	2.61 C-2	1.9	2.00
3	1.0 A-1	0.1	2.12 C-1	1.85	1.53
3 A	1.0 A-1	0.1	2.12 C-2	1.85	1.51
4	1.0 A-2	/	2.0 C-1	2.0	3.59
4 A	1.0 A-2	/	2.0 C-2	2.0	3.54
5	1.0 A-1	0.1	2.19 C-1	1.9	1.74
5 A	1.0 A-1	0.1	2.19 C-2	1.9	1.69
6	1.0 A-1	0.25	2.47 C-1	1.8	1.72
6 A	1.0 A-1	0.25	2.47 C-2	1.8	1.62
7	1.0 A-3	/	2.0 C-1 A	2.0	2.06
7 A	1.0 A-3	/	2.0 C-2	2.0	2.19
8	1.0 A-4	/	2.0 C-1 A	2.0	3.24
8 A	1.0 A-4	/	2.0 C-2	2.0	3.29

*TMP = trimethylolpropane

Table 2

	Wetting	Crystallization	Strength in N/mm ²		
	(sec.)	(sec.)	after 24 hours	7 days	
5	1	25	75	5.0	12.6
	1 A	65	120	8.1	15.0
	2	60	85	6.0	14.6
	2 A	100	150	8.3	15.1
10	3	45	70	/	/
	3 A	70	115	/	/
	5	/	/	5.0	13.0
	5 A	/	/	8.9	14.8
15	7	/	/	0.2	3.4
	7 A	/	/	1.8	3.8
	8	/	/	2.0	3.1
	8 A	/	/	1.8	8.2

The tests denoted by A were each comparative tests. The more rapid initial solidification of the hot melt systems based on crystalline polyesters (1-3) according to the invention can clearly be seen.

Table 3

	Adhesive	Viscosity (Pas) at 120°C after storage for		
		0 hours	24 hours	72 hours
5	1	9.0	/	/
	1 A	22.0	/	/
	2	5.0	16.0	28.0
	2 A	15.0	145.0	596.0
	3	13.0	/	/
10	3 A	35.0	/	/
	4	2.8	6.1	13.4
	4 A	4.4	13.3	67.9
	5	6.0	12.0	20.0
	5 A	19.0	80.0	242.0
15	6	6.8	17.5	72.0
	6 A	24.0	240.0	crosslinked
	7	5.0	7.6	12.0
	7 A	7.8	18.0	58.0
	8	6.7	17.0	64.0
20	8 A	8.5	16.0	crosslinked

The lower initial viscosity and the reduced increase in viscosity at elevated temperature after the period of storage can clearly be seen for the hot melt systems according to the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A reactive hot melt containing isocyanate groups and having a low initial viscosity and enhanced temperature stability, comprising

(i) a hydroxypolyol containing ester or ether groups, with a hydroxyl number of 15 to 150 and an average functionality of 1.95 to 2.2, and

(ii) a diphenylmethane diisocyanate with a ratio of isocyanate groups in (ii) to hydroxyl groups in (i) of 1.4:1 to 2.5:1, characterized in that the diphenylmethane diisocyanate has a content of at least 70 weight % of 2,4'-isomers.

2. A reactive hot melt according to claim 1, characterized in that component (i) is a crystalline hydroxypolyester polyol.

3. A reactive hot melt according to claim 1, characterized in that component (i) is an amorphous hydroxypolyester polyol.

4. A reactive hot melt according to any one of claims 1 to 3, characterized in that component (ii) comprises a diphenylmethane diisocyanate having a 2,4'-isomer content of more than 85 weight %.

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